

Amendment

TOWNSEND and TOWNSEND and CREW LLP

Two Embarcadero Center, 8<sup>th</sup> Floor  
San Francisco, California 94111-3834  
(303) 571-4000

In re application of: CHAU NGUYEN et al.

Application No.: 09/190,961

Filed: November 12, 1998

Group Art Unit: 1763

For: LIQUID PHOSPHOROUS PRECURSOR DELIVERY APPARATUS

THE ASSISTANT COMMISSIONER FOR PATENTS  
U. S. Patent and Trademark Office  
Washington, D.C. 20231

Attorney Docket No. 16301-002010US

Client Ref No. 000888 USA C01/PDD/KPU8/JW

Date: September 06, 2000

I hereby certify that this is being deposited with the United States Postal Service as first class mail in an envelope addressed to:

Assistant Commissioner for Patents  
U. S. Patent and Trademark Office  
Washington, D.C. 20231

Signed: Sara B. McPeak  
Sara B. McPeak

Sir:

Transmitted herewith is an amendment in the above-identified application.

- ☒ Enclosed also is an Affidavit of the inventor under 37 CFR § 1.132.  
☐ Small entity status of this application under 37 CFR 1.9 and 1.27 has been established by a verified statement previously submitted.  
☐ A verified statement to establish small entity status under 37 CFR 1.9 and 1.27 is enclosed.

If any extension of time is needed, then this response should be considered a petition therefor.

- The filing fee has been calculated as shown below

(Col. 1)	(Col. 2)	(Col. 3)
CLAIMS REMAINING AFTER AMENDMENT	HIGHEST NO. PREVIOUSLY PAID FOR	PRESENT EXTRA
TOTAL * 31	MINUS ** 31	= 0
INDEP. * 6	MINUS *** 6	= 0
[ ] FIRST PRESENTATION OF MULTIPLE DEP. CLAIM		

SMALL ENTITY	
RATE	ADDIT. FEE
x \$9.00 =	
x \$39.00 =	
+ \$130.00 =	
TOTAL ADDIT. FEE	

OR

OTHER THAN SMALL ENTITY	
RATE	ADDIT. FEE
x \$18.00 =	\$0.00
x \$78.00 =	\$0.00
+ \$200.00 =	
TOTAL	\$0.00

OR

- \* If the entry in Col. 1 is less than the entry in Col. 2, write "0" in Col. 3.  
\*\* If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, write "20" in this space.  
\*\*\* If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, then write "3" in this space. The "Highest Number Previously Paid For" (Total or Independent) is the highest number found from the equivalent box in Col. 1 of a prior amendment or the number of claims originally filed.

[ X ] No fee is due.

Please charge Deposit Account No. 20-1430 as follows:

[ X ] Any additional fees associated with this paper or during the pendency of this application.

NO extra copies of this sheet are enclosed.

TOWNSEND and TOWNSEND and CREW LLP

Roger T. Barrett  
Roger T. Barrett, Reg. No.: 41,599  
Attorneys for Applicant



**PATENT**  
Attorney Docket No. 16301-002010US  
Client Ref No. 000888 USA C01/PDD/KPU8/JW

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re application of:

Chau Nguyen et al.

Application No.: 09/190,961

Filed: November 12, 1998

CPA filed: May 1, 2000

For: LIQUID PHOSPHOROUS  
PRECURSOR DELIVERY APPARATUS

Examiner:: Richard Bueker

Art Unit: 1763

**AFFIDAVIT OF VISWESWAREN  
SIVARAMAKRISHNAN UNDER 37  
C.F.R. § 1.132**

**BOX AF**  
Assistant Commissioner for Patents  
Washington, D.C. 20231

Sir:

I am a joint inventor of the above-referenced patent application.

In various systems, such as a chemical vapor deposition system used to process semiconductor wafers, valves may be used to deliver certain types of reactants, also known as precursors, to the deposition chamber. As described in the specification on page 5, prior-art valves are made of SST 316, including valves used by Applied Materials, Inc., assignee of the present invention and the world's largest producer of semiconductor wafer processing equipment. "Nickel-containing" stainless steels, such as SST 316, are generally preferred for use in wafer processing equipment as these stainless steels are known to have good corrosion resistance, be easily cleaned, be easily welded, and can operate over a very wide temperature range, including cryogenic temperatures.

When these valves are used to deliver a phosphorous-containing precursor, the valves can become clogged with residue after processing about 1800 wafers. We desired to increase the throughput of wafers between scheduled maintenance (cleaning) of the valves to increase the up-time of deposition systems that used phosphorous precursors, but did not know which aspects of the phosphorous precursor delivery system contributed to the residue build-up.

Nguyen et al.  
Application No.: 09/190,961  
Page 2

PATENT

Our first effort to improve up-time was to replace certain components in the standard delivery valve with components made from HASTELLOY™, which is considered to be more corrosion resistant than SST 316. To our surprise, residue built up even more quickly with the HASTELLOY valve than with the valve fabricated from SST 316. We noted that one difference between the two metals was that HASTELLOY has a higher nickel content (approximately 52%) than SST 316 (approximately 12-15% nickel).

We guessed that nickel may help decompose the phosphorous precursor and contribute to the build up of residue, as stated on page 5, lines 15-16 of the specification. We verified our suspicions through a series of tests, as stated on page 5, lines 4-6, that the amount of nickel in an alloy in contact with liquid TEPO, one common type of phosphorous precursor, did affect residue build-up.

The first set of tests were "beaker" tests, in which approximately 300 cc of TEPO was placed in a quartz ampule with a 1" X 1" coupon of the metal being tested. The sample was heated to approximately 150 °C, and the TEPO was observed for changes over a standard time period. The test was repeated on samples of HASTELLOY, SST 316, SST 430, SST 440, and SST 446 using the same procedures and test conditions for all of the metal samples being tested. The TEPO was originally colorless, but changed to light yellow, to dark yellow, to yellowish red depending upon the nickel content of the sample being tested. Additionally, the pH of the TEPO was measured after a selected time, a greater change in the pH indicating greater decomposition of the TEPO by the metal sample. The decomposition of TEPO was much less with SST 430, SST 440, and SST 446, all low-nickel alloys, than with HASTELLOY or SST 316. The decomposition of TEPO was less with SST 316 than HASTELLOY. These tests convinced us that a trend existed, namely, that the amount of nickel in components contacting the liquid precursor compound directly affected the amount of residue build-up on those components. The lower the nickel content, the less build up would occur.

We concluded that to reduce residue build up, metal components in contact with a phosphorous precursor should be made from an alloy with less nickel content than the present SST 316 components. Since SST 316 may have as little as 10% nickel according to the Chemical Composition chart attached hereto as Exhibit A, use of any steel alloy having less than 10% nickel would produce improved results.

Nguyen et al.  
Application No.: 09/190,961  
Page 3

PATENT

To verify our unexpected conclusion, we performed an additional experiment in the series of tests at substantially greater cost. For these additional tests, parts for a delivery valve were manufactured from SST 430. SST 430 was chosen because SST 430 is less expensive and generally easier to machine than SST 440 and SST 446, although from our beaker tests we believed we would obtain similar results from parts fabricated from SST 440 or SST 446, which both have nominally about 0.6% nickel. It should be noted that, although the SST 430 we used to fabricate a valve from had approximately 0.15% nickel, SST 430 may have up to 0.75% nickel, as shown on the attached Chemical Composition chart provided by the Stainless Steel Industry of North America (Exhibit A). Additionally, since our tests established a trend, I believe that steel alloys with lower nickel content than currently used SST 316 (i.e., less than 10% nickel), also would lessen residue buildup.

As described on page 5, lines 8-14, a valve made from SST 430 was fabricated and used to control the flow of TEPO for 189 hours without clogging, at which time the experiment was terminated. This experiment was performed at approximately the same temperature and flow rate as would be seen in a manufacturing environment, and is equivalent to processing 11,300 wafers. These conditions were consistent with the conditions that caused clogging of the SST 316 valve after only 1,800 wafers. Therefore, I believe the experiment held all critical parameters essentially constant except for the nickel concentration in the valve, and verified that residue build-up is affected by the nickel concentration of a metal alloy in contact with the phosphorous precursor. I believe that this property, the decomposition of phosphorous precursor by nickel in a metal alloy in contact with the precursor, was not a recognized or expected property of any stainless steel or similar metal alloy.

Based on these test results and as described in our patent application, any reduction in the nickel content from the present SST 316 alloy appears to be superior when used to fabricate components that come in contact with a phosphorous precursor. Hence, any steel alloy with less than 10% nickel is believed to produce improved results.

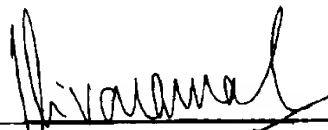
Nguyen et al.  
Application No.: 09/190,961  
Page 4

PATENT

Furthermore, stainless steel alloys having a nickel concentration less than that of the standard SST 316 would not have been obvious to use for a phosphorous precursor delivery system. As previously noted, Austenitic, also called "nickel-containing", stainless steels such as SST 316 are generally preferred for use in wafer processing equipment due to a myriad of benefits, including good corrosion resistance. This is one reason why we initially tested a higher nickel content steel (HASTELLOY) in an attempt to lessen residue buildup. Therefore, without the understanding that the nickel concentration affects the breakdown of phosphorous precursor, there would be no motivation to replace the SST 316 of the prior valve with a low-nickel alloy.

Based upon my personal knowledge and belief, I declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like are punishable by fine or imprisonment, or both under §1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the patent application or any patent issuing thereon.

Executed on 9/5/00 at Santa Clara, California.



Visweswaren Sivaramakrishnan